The role of deep centers in formation of luminescent and dosimetric properties of wide-gap materials

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Abstract. The direct and indirect methods of experimental detection of deep traps in wide-gap insulators are described. The experimentally observed effects of influence of deep traps with different nature on luminescent and dosimetric properties of materials are analyzed. It is established that the most wide-spread and well-studied effects are the sensitization and superlinearity of dose response. They are interpreted in terms of the kinetic model of competitive electron traps. Taking into account the temperature dependence of capture probability by deep traps in this model allows one to explain some new effects associated with luminescence thermal quenching. The luminescence model of Al_2O_3:C single crystal is described. In this model the temperature dependence of competitive interaction between the main and deep traps is caused by thermal ionization of excited states of F-centers.

1. Introduction

The mechanisms and features of thermoluminescence (TL) in different materials are studied in terms of necessity of solution of fundamental and applied tasks associated with its application in radiation dosimetry, geology, archaeology and temperature sensing. In a simple TL model only two localized levels are taken into account: an electron trap and recombination center. The development of this model is an account of the competing effects of deep trapping centers. The deep centers are traps with energy depth more than in the main dosimetric ones which remain thermally stable and not emptied during usual TL registration. The available literature information about the role of deep centers in the TL mechanism in different materials has an odd and non-systemized character. In this regard, the aim of this work is to reveal general regularities and mechanisms of effect of deep traps on luminescent and dosimetric properties of wide-gap materials on the base of the analysis of available experimental data and kinetic models of TL.

2. Experimental methods of deep traps detection

Experimental difficulties in deep traps detection by direct measurement of high-temperature TL peaks are due to the presence of significant thermal radiation of the heating element at T>400 ^{o}C. In some cases it is possible to observe the TL peaks associated with deep traps after high-dose irradiation of the material. The high temperature TL peaks were registered after excitation of LiF:Mg,Ti; LiF:Mg,Cu,P and Al_2O_3:C by different types of ionizing radiation [1-3]. In Al_2O_3:C intensive TL peaks of deep traps at T=300-600 ^{o}C are also observed after excitation by unfiltered UV-radiation of a mercury lamp at high temperatures [4]. In this case the traps are filled by optical ionization of F-centers. The probability of this process increases with the temperature growth. The concentration of F-centers in Al_2O_3:C is high (10^{17} cm^{-3}), resulting in high efficiency of deep traps filling in this way.

The indirect methods of deep traps detection include the observation of the phototransferred thermoluminescence (PTTL) peaks. For registration of a PTTL signal a sample is pre-irradiated by ionizing radiation which fills the deep traps. After thermal empting of the main traps the optical transfer of charge carriers from deep traps to shallow ones occurs. The main shallow traps give PTTL peaks after further thermal stimulation. PTTL is experimentally observed in many materials: SiO_2; LiF:Mg,Ti; CaF_2:Mn; Al_2O_3:C [5-8]. A simple kinetic PTTL model includes two electron traps (main and deep) and a recombination center. The development of these concepts is a model which takes into account optical bleaching of the main traps TL occurring simultaneously with the empting of deep centers [5]. The model has allowed one to explain non-monotonic dependence of the PTTL intensity versus photostimulation time observed experimentally, in particular, in Al_2O_3:C and SiO_2 [5,9]. There are other indirect methods to prove the existence of deep trapping centers in dosimetric materials based on the detection of the effects of sensitization and superlinearity of dose response. Experimental manifestations and mechanisms of these effects will be discussed below.

3. Models of competing interaction of trapping centers involving deep traps in wide-gap insulators

3.1. The model of competitive electron traps

The model contains the main TL-active trap, deep trap and recombination center. Excitation of phosphor leads to the formation of the electron-hole pairs. Resulting free charge carriers can be captured at localized levels. During the subsequent thermal stimulation the captured electrons are released from active traps in the conduction band. Then free electrons can recombine with holes at the luminescent centre accompanied by generation of photons. Another possibility is to capture electrons by a deep trap. The situation when charge carriers released into the conduction band from one center can be captured by another trap is considered to be the interaction of these traps. This is the so-called interactive kinetics of TL [10].

The most important practical application of the model considered is the explanation of the effect of superlinearity of dose response. The term "superlinearity” means faster than linear dependence on the dose. The effect of superlinearity is observed in different dosimetric materials [11-13] and can occur in the whole range of registered doses, and in some parts of dose dependences. In theoretical works [14-16] the analyzed model is considered in two stages of TL signal formation: excitation and heating. It is shown that the gradual filling of competitive deep traps with increasing doses reduces the probability of capturing electrons and increases the number of recombination acts at the luminescent centre that causes superlinearity. Other authors considered two types of active traps in terms of the model of competing traps. They are interactive (interacting with the deep traps) and non-interactive [17]. This modified model was used to calculate superlinearity of TL dose response of peak 5 in LiF:Mg,Ti [18].

The effect of increasing the sensitivity of phosphor to radiation (sensitization effect) is associated with the superlinearity of dose response. The sensitivity is TL response to low test dose. Sensitization in repeated irradiation-heating cycles is observed, in particular, for the TL peak at 110 ^{o}C in quartz. It can be described in terms of the model of competing electron traps [19]. As a rule, the effect of sensitization is observed in the same dose range as the superlinearity and characterized by a similar mechanism associated with competing capture of charge carriers by deep traps.

We modified the model under study by consideration of the temperature dependence of the probability of capturing by deep traps, which was observed experimentally for Al_2O_3:C single crystals [4]. Alongside with the phenomena of superlinearity and sensitization, this model has allowed us to explain new experimentally observed effects [4,13], in particular, the influence of the heating rate on the degree of dose responses superlinearity (figure 1).

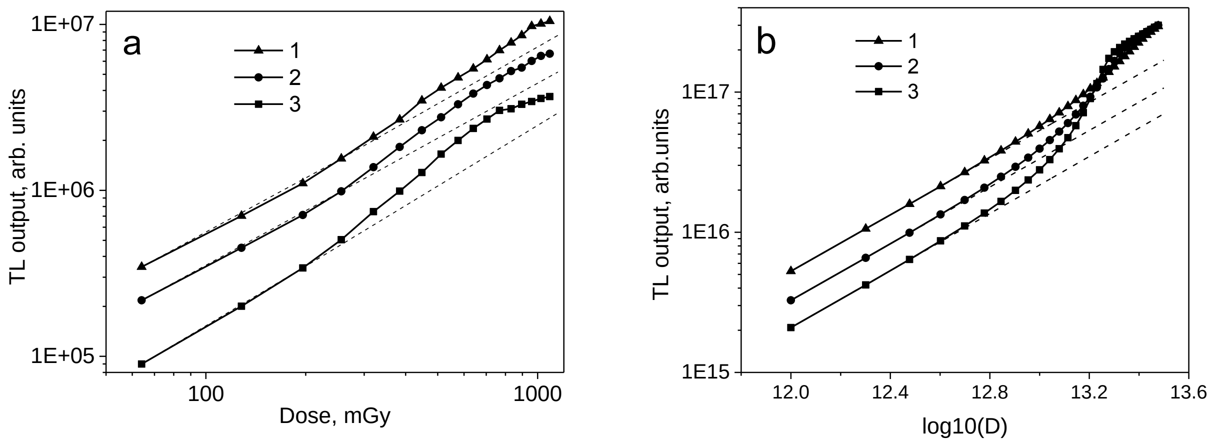

Figure 1. Experimental (a) [13] and calculated (b) [20] dose dependences of the main TL peak in Al_2O_3:C at heating rates of 0.5 (1), 2(2) and 6 K/s

3.2. The models taking into account the deep hole traps

The kinetic model is analyzed [21] which takes into account the competition between the recombination centers, which may be regarded as deep hole traps. It is shown that the competition between the hole centers at a excitation stage gives rise to the effect of dose response superlinearity. In addition, this model explains the dose-rate dependence of the TL intensity and anomalous fading [22,23].

A more complex model which includes two electron and two hole centers is described in literature [24]. This model explains the appearance of non-monotonic dose dependence, experimentally observed in some phosphors (LiF:Mg,Ti; Al_2O_3:C; natural quartz) [25-27]. In this case, the TL output increases with a growing dose, reaching the maximum, and then decreases. An important conclusion made by the authors is that non-monotonic dose dependence in the range of high doses can be caused not only by radiation destruction of active centers but their competitive interaction.

Deep traps capable of capturing the charge carriers with a different sign, are identified in Al_2O_3:C single crystals. In particular, the sensitization/desensitization effects after annealing of the samples preliminary irradiated by UV-radiation [28] and a pulsed electron beam [3] are analyzed. It was found that at temperature ranges of 350-500 ^{o}C and 650-750 ^{o}C mainly electron traps are emptied. The hole traps are active at T=500-650 ^{o}C and T>700 ^{o}C. The obtained results agree in the main with those of other authors [26,29] who used other ways of deep centers filling.

According to the nature of the deep traps in Al_2O_3:C kinetic models are proposed which take into account the competing capture of electrons and their non-radiative recombination with holes on the electron and hole deep traps respectively. In literature [30,31] a model which includes one electron and one hole deep trap, is analyzed at the stage of UV and ionizing radiation excitation, as well as thermal stimulation. It is found that this model provides a good quantitative description of the dose dependence of the TL output in the main peak and concentration of luminescent centers. In our paper [28] it is shown that the additional account of the temperature dependence of the probability of capturing by deep electron traps allows one to describe not only the effects of changes in sensitivity, but also the influence of the occupancy of deep traps of different nature on the dependence of TL output in dosimetric peak on a heating rate (figure 2). A significant role of deep traps in heating-rate effect in Al_2O_3 samples with oxygen vacancies created not only by thermal but also radiative coloration, as well as for nanostructured modification was further established [32,33]. In our paper [34] the model was supplemented by taking into account the hole traps contributing to the broadening of the main TL peak at 180 ^{o}C. In terms of the modified model the sensitization/desensitization effects were analyzed in Al_2O_3:C samples with different half-width of the main TL peak.

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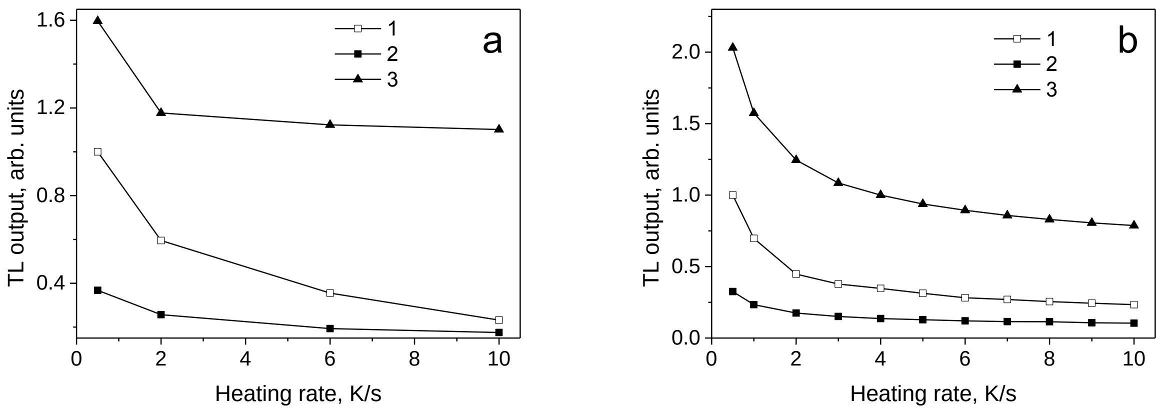

Figure 2. Experimental (a) and calculated (b) dependence of the TL output in the main peak on the heating rate for different states of deep traps [28]: 1 - deep traps are emptied; 2 – deep hole traps are partially occupied; 3 - deep electron traps are partially occupied

3.3. A model of thermal quenching of luminescence in Al_2O_3:C single crystals taking into account thermal ionization of F-centers

The disadvantage of previously considered kinetic models describing the TL mechanism in wide-gap materials is lack of consideration of the energy structures of the particular defects (traps and luminescent centers). We proposed the model [35] which describes the mechanism of luminescence in Al_2O_3:C single crystals. This model, along with competing capture of charge carriers by deep traps, takes into account the thermal ionization of excited states of luminescent centers (F-centers) (figure 3).

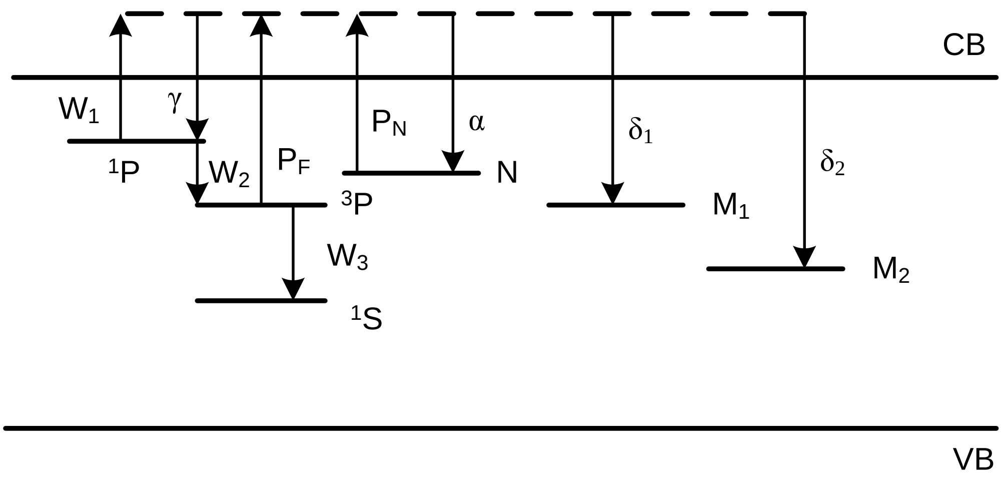

Figure 3. The energy band diagram of the luminescence model in Al_2O_3:C taking into account the thermal ionization of F-centers [35]

In this figure N is the main (dosimetric) trap, M_1, M_2 are deep electron traps, ^1S - ground state, ^1P, ^3P - excited levels of F-center. The ^1P level is near the bottom of the conduction band, so the probability of W_1 transition is assumed to be independent on temperature. Thermal ionization of the excited state (^3P) corresponds to the P_F transition, probability of which increases exponentially during heating of the sample. The ionization of F-center results in formation of F^+-center which after electron capture (transition γ) could once again become an excited F-center. Luminescence of F-center (3.0 eV)

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corresponds to the W_3 transition. During the excitation by ionizing radiation free charge carriers are generated which are captured by the traps. During the subsequent thermal stimulation the electrons released from trap N are captured by F^+-center, forming an excited F-center. Then free electrons formed by ionization of excited (^3P) state of F-center may be captured by the deep traps. Thus, in this model the main and deep trapping centers are considered in an interactive relationship.

The simulation results show [35] that the process of thermal ionization of excited states of F-centers leads to a decrease in the share of radiative transitions inside the centre and the increase in the probability of electron capturing by deep traps. These effects cause thermal quenching of photo - and radioluminescence in the crystals under study. In addition, the shape of the calculated quenching curves depends on the degree of deep traps filling (figure 4), which was observed experimentally [36]. The proposed model also explains the described earlier regularities of influence of deep electron traps occupancy on TL sensitivity and the degree of its dependence on the heating rate, as well as on the shape of the main TL peak [35]. Later this model and its modifications were used to analyze the effects of optically stimulated luminescence and thermally stimulated conductivity in Al_2O_3:C [37].

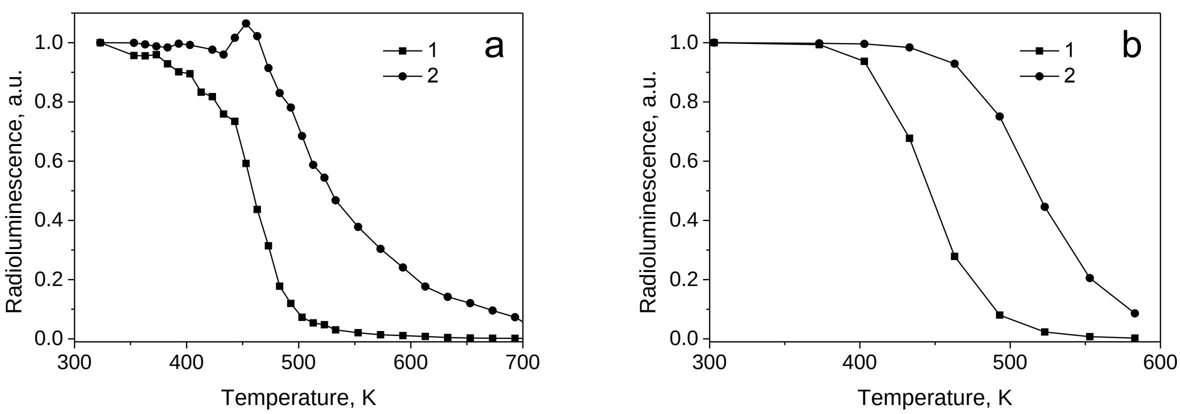

Figure 4. Experimental (a) and calculated (b) thermal quenching curves of F-centers radioluminescence in Al_2O_3:C for two states of deep traps occupancy [35]: 1 - deep traps are emptied; 2 – deep electron traps are partially occupied

4. Conclusions

Deep trapping centers in wide-gap insulators can be experimentally detected by the method of direct observation of the high-temperature TL peaks as well as by a number of indirect methods. Competing influence of deep electron traps causes the effects of sensitization and superlinearity of TL dose response. Taking into account the effects of hole centres allows one to explain a number of new effects, such as non-monotonic behaviour of the TL output with increasing dose, its dose-rate dependence, and anomalous fading. The nature of deep traps which cause sensitization/desensitization effects in Al_2O_3:C single crystals was analyzed. Consideration of the temperature dependence of the capture probability by deep traps allows one to explain new effects in this material. These effects are associated with the influence of deep centers occupancy on luminescence quenching, the dependence of TL output and degree of superlinearity of dose response on heating rate. The model describing the luminescence mechanism in Al_2O_3:C with regard to the process of thermal ionisation of excited states of F-centers is proposed.

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